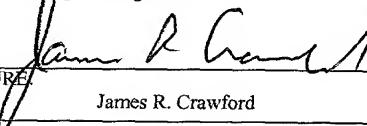


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|--|--|--|--|---|
| FORM PTO 1390<br>(REV 11-2000)   |  | U S DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE |  | ATTORNEY'S DOCKET NUMBER<br>DNAG 228 - PFF/JRC                    |
| TRANSMITTAL LETTER TO THE UNITED STATES<br>DESIGNATED/ELECTED OFFICE (DO/EO/US)<br>CONCERNING A FILING UNDER 35 U.S.C. 371   |  |  |  | US APPLICATION NO. (If known, see 37 CFR 1.5)<br><b>10/009099</b> |
| INTERNATIONAL APPLICATION NO.<br><b>PCT/EP00/02872</b>   | INTERNATIONAL FILING DATES<br><b>31 March 2000</b> | PRIORITY DATE CLAIMED<br><b>9 June 1999</b>            |  |   |
| TITLE OF INVENTION<br><b>METHOD FOR PRODUCING BARIUM SULFATE, BARIUM SULFATE AND THE UTILIZATION THEREOF</b>   |  |  |  |   |
| APPLICANT(S) FOR DO/EO/US <b>AMIRZADEH-ASL, et al.</b>   |  |  |  |   |
| Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:  |  |  |  |   |
| <p>1. <input checked="" type="checkbox"/> This is a <b>FIRST</b> submission of items concerning a filing under <u>35 U.S.C. 371</u>.</p> <p>2. <input type="checkbox"/> This is a <b>SECOND</b> or <b>SUBSEQUENT</b> submission of items concerning a filing 35 U.S.C. 371</p> <p>3. <input checked="" type="checkbox"/> This is an express request to begin national examination procedures (35 U.S.C. 371 (f)). The submission must include items (5), (6), (9) and (21) indicated below.</p> <p>4. <input type="checkbox"/> The US has been elected by the expiration of 19 months from the priority date (PCT Article 31).</p> <p>5. <input checked="" type="checkbox"/> A copy of the International Application as filed (35 U.S.C. 371 (c)(2))<br/>       a. <input checked="" type="checkbox"/> is attached hereto (required only if not communicated by the International Bureau).<br/>       b. <input checked="" type="checkbox"/> has been communicated by the International Bureau.<br/>       c. <input type="checkbox"/> is not required, as the application was filed in the United States Receiving Office (RO/US).</p> <p>6. <input checked="" type="checkbox"/> An English language translation of the International Application as filed (35 U.S.C. 371 (c)(2))<br/>       a. <input checked="" type="checkbox"/> is attached hereto.<br/>       b. <input type="checkbox"/> has been previously submitted under 35 U.S.C. 154(d)(4).</p> <p>7. <input checked="" type="checkbox"/> Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371 (c)(3))<br/>       X <input type="checkbox"/> are attached hereto (required only if not communicated by the International Bureau).<br/>       b. <input type="checkbox"/> have been communicated by the International Bureau.<br/>       c. <input type="checkbox"/> have not been made; however, the time limit for making such amendments has NOT expired.<br/>       d. <input type="checkbox"/> have not been made and will not be made.</p> <p>8. <input type="checkbox"/> An English language translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371 (c)(3)).</p> <p>9. <input type="checkbox"/> An oath or declaration of the inventor(s) (35 U.S.C. 371 (c)(4)).</p> <p>10. <input type="checkbox"/> An English language translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371 (c)(5)).</p> |  |  |  |   |
| Items 11 to 20 below concern document(s) or information included:  |  |  |  |   |
| <p>11. <input checked="" type="checkbox"/> An Information Disclosure Statement under 37 CFR 1.97 and 1.98.</p> <p>12. <input type="checkbox"/> An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.</p> <p>13. <input checked="" type="checkbox"/> A <b>FIRST</b> preliminary amendment.</p> <p>14. <input type="checkbox"/> A <b>SECOND</b> or <b>SUBSEQUENT</b> preliminary amendment.</p> <p>15. <input type="checkbox"/> A substitute specification.</p> <p>16. <input type="checkbox"/> A change of power of attorney and/or address letter.</p> <p>17. <input type="checkbox"/> A computer-readable form of the sequence listing in accordance with PCT Rule 13ter.2 and 35 U.S.C. 1.821 - 1.825.</p> <p>18. <input type="checkbox"/> A second copy of the published international application under 35 U.S.C. 154(d)(4).</p> <p>19. <input type="checkbox"/> A second copy of the English language translation of the international application under 35 U.S.C. 154(d)(4).</p> <p>20. <input type="checkbox"/> Other items or information: PCT/IPEA/416; PCT/ISA/210</p>   |  |  |  |   |

03 DEC 2001

| U.S. APPLICATION NO. (if known, see 37 CFR 1.5)   | INTERNATIONAL APPLICATION NO | ATTORNEY'S DOCKET NUMBER   |                                  |              |              |      |              |        |   |      |                    |       |   |      |   |  |   |    |                                      |  |  |            |   |  |  |    |                   |  |  |            |  |  |  |    |   |  |  |    |                             |  |  |            |   |  |  |         |                              |  |  |            |  |  |  |                                  |  |  |  |                    |
|---|------------------------------|--|----------------------------------|--------------|--------------|------|--------------|--------|---|------|--------------------|-------|---|------|---|--|---|----|--------------------------------------|--|--|------------|---|--|--|----|-------------------|--|--|------------|--|--|--|----|---|--|--|----|-----------------------------|--|--|------------|---|--|--|---------|------------------------------|--|--|------------|--|--|--|----------------------------------|--|--|--|--------------------|
| <b>10/009099</b>  | PCT/EP00/02872               | DNAG 228-PFF/JRC   |                                  |              |              |      |              |        |   |      |                    |       |   |      |   |  |   |    |                                      |  |  |            |   |  |  |    |                   |  |  |            |  |  |  |    |   |  |  |    |                             |  |  |            |   |  |  |         |                              |  |  |            |  |  |  |                                  |  |  |  |                    |
| 17. <input checked="" type="checkbox"/> The following fees are submitted:   |                              | CALCULATIONS PTO USE ONLY  |                                  |              |              |      |              |        |   |      |                    |       |   |      |   |  |   |    |                                      |  |  |            |   |  |  |    |                   |  |  |            |  |  |  |    |   |  |  |    |                             |  |  |            |   |  |  |         |                              |  |  |            |  |  |  |                                  |  |  |  |                    |
| <b>BASIC NATIONAL FEE (37 CFR 1.492 (a) (1) - (5)):</b>   |                              |  |                                  |              |              |      |              |        |   |      |                    |       |   |      |   |  |   |    |                                      |  |  |            |   |  |  |    |                   |  |  |            |  |  |  |    |   |  |  |    |                             |  |  |            |   |  |  |         |                              |  |  |            |  |  |  |                                  |  |  |  |                    |
| <input type="checkbox"/> Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO ..... \$1040.00<br><input checked="" type="checkbox"/> International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO ..... \$890.00<br><input type="checkbox"/> International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International search fee (37 CFR 1.445(a)(2)) paid to USPTO ..... \$740.00<br><input type="checkbox"/> International preliminary examination fee (37 CFR 1.482) paid to USPTO but all claims did not satisfy provisions of PCT Article 33(1)-(4) ..... \$710.00<br><input type="checkbox"/> International preliminary examination fee (37 CFR 1.482) paid to USPTO and all claims satisfied provisions of PCT Article 33(1)-(4) ..... \$100.00  |                              |  |                                  |              |              |      |              |        |   |      |                    |       |   |      |   |  |   |    |                                      |  |  |            |   |  |  |    |                   |  |  |            |  |  |  |    |   |  |  |    |                             |  |  |            |   |  |  |         |                              |  |  |            |  |  |  |                                  |  |  |  |                    |
| <b>ENTER APPROPRIATE BASIC FEE AMOUNT =</b>   |                              |  |                                  |              |              |      |              |        |   |      |                    |       |   |      |   |  |   |    |                                      |  |  |            |   |  |  |    |                   |  |  |            |  |  |  |    |   |  |  |    |                             |  |  |            |   |  |  |         |                              |  |  |            |  |  |  |                                  |  |  |  |                    |
| \$ 890.00   |                              |  |                                  |              |              |      |              |        |   |      |                    |       |   |      |   |  |   |    |                                      |  |  |            |   |  |  |    |                   |  |  |            |  |  |  |    |   |  |  |    |                             |  |  |            |   |  |  |         |                              |  |  |            |  |  |  |                                  |  |  |  |                    |
| Surcharge of \$ 130.00 for furnishing the oath or declaration later than  |                              |  |                                  |              |              |      |              |        |   |      |                    |       |   |      |   |  |   |    |                                      |  |  |            |   |  |  |    |                   |  |  |            |  |  |  |    |   |  |  |    |                             |  |  |            |   |  |  |         |                              |  |  |            |  |  |  |                                  |  |  |  |                    |
| <input type="checkbox"/> 20 <input checked="" type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492 (e)).<br><table border="1" style="width: 100%; border-collapse: collapse;"> <thead> <tr> <th>CLAIMS</th> <th>NUMBER FILED</th> <th>NUMBER EXTRA</th> <th>RATE</th> </tr> </thead> <tbody> <tr> <td>Total claims</td> <td>7-20 =</td> <td>0</td> <td>X \$</td> </tr> <tr> <td>Independent claims</td> <td>1-3 =</td> <td>1</td> <td>X \$</td> </tr> <tr> <td>MULTIPLE DEPENDENT CLAIM(s) (if applicable)</td> <td></td> <td>X</td> <td>\$</td> </tr> <tr> <td colspan="3" style="text-align: center;"><b>TOTAL OF ABOVE CALCULATIONS =</b></td> <td style="text-align: right;">\$ 1020.00</td> </tr> <tr> <td colspan="3"> <input checked="" type="checkbox"/> Applicant claims small entity status. See 37 CFR 1.27. The fees indicated above are reduced by ½.         </td> <td style="text-align: right;">\$</td> </tr> <tr> <td colspan="3" style="text-align: right;"><b>SUBTOTAL =</b></td> <td style="text-align: right;">\$ 1020.00</td> </tr> <tr> <td colspan="3">Processing fee of \$ _____ for furnishing the English translation later than</td> <td style="text-align: right;">\$</td> </tr> <tr> <td colspan="3"> <input type="checkbox"/> 20 <input checked="" type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492 (f)). + _____         </td> <td style="text-align: right;">\$</td> </tr> <tr> <td colspan="3" style="text-align: right;"><b>TOTAL NATIONAL FEE =</b></td> <td style="text-align: right;">\$ 1020.00</td> </tr> <tr> <td colspan="3">Fee for recording the enclosed assignment (37 CFR 1.21 (h)). Assignment Must be accompanied by appropriate cover sheet (37 CFR 3.28, 3.31) ( per property).</td> <td style="text-align: right;">+ \$ 00</td> </tr> <tr> <td colspan="3" style="text-align: right;"><b>TOTAL FEES ENCLOSED =</b></td> <td style="text-align: right;">\$ 1020.00</td> </tr> <tr> <td colspan="3"></td> <td style="text-align: right;"><b>Amount to be Refunded:</b> \$</td> </tr> <tr> <td colspan="3"></td> <td style="text-align: right;"><b>Charged:</b> \$</td> </tr> </tbody></table> |                              |  | CLAIMS                           | NUMBER FILED | NUMBER EXTRA | RATE | Total claims | 7-20 = | 0 | X \$ | Independent claims | 1-3 = | 1 | X \$ | MULTIPLE DEPENDENT CLAIM(s) (if applicable) |  | X | \$ | <b>TOTAL OF ABOVE CALCULATIONS =</b> |  |  | \$ 1020.00 | <input checked="" type="checkbox"/> Applicant claims small entity status. See 37 CFR 1.27. The fees indicated above are reduced by ½. |  |  | \$ | <b>SUBTOTAL =</b> |  |  | \$ 1020.00 | Processing fee of \$ _____ for furnishing the English translation later than |  |  | \$ | <input type="checkbox"/> 20 <input checked="" type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492 (f)). + _____ |  |  | \$ | <b>TOTAL NATIONAL FEE =</b> |  |  | \$ 1020.00 | Fee for recording the enclosed assignment (37 CFR 1.21 (h)). Assignment Must be accompanied by appropriate cover sheet (37 CFR 3.28, 3.31) ( per property). |  |  | + \$ 00 | <b>TOTAL FEES ENCLOSED =</b> |  |  | \$ 1020.00 |  |  |  | <b>Amount to be Refunded:</b> \$ |  |  |  | <b>Charged:</b> \$ |
| CLAIMS  | NUMBER FILED                 | NUMBER EXTRA   | RATE                             |              |              |      |              |        |   |      |                    |       |   |      |   |  |   |    |                                      |  |  |            |   |  |  |    |                   |  |  |            |  |  |  |    |   |  |  |    |                             |  |  |            |   |  |  |         |                              |  |  |            |  |  |  |                                  |  |  |  |                    |
| Total claims  | 7-20 =                       | 0  | X \$                             |              |              |      |              |        |   |      |                    |       |   |      |   |  |   |    |                                      |  |  |            |   |  |  |    |                   |  |  |            |  |  |  |    |   |  |  |    |                             |  |  |            |   |  |  |         |                              |  |  |            |  |  |  |                                  |  |  |  |                    |
| Independent claims  | 1-3 =                        | 1  | X \$                             |              |              |      |              |        |   |      |                    |       |   |      |   |  |   |    |                                      |  |  |            |   |  |  |    |                   |  |  |            |  |  |  |    |   |  |  |    |                             |  |  |            |   |  |  |         |                              |  |  |            |  |  |  |                                  |  |  |  |                    |
| MULTIPLE DEPENDENT CLAIM(s) (if applicable)   |                              | X  | \$                               |              |              |      |              |        |   |      |                    |       |   |      |   |  |   |    |                                      |  |  |            |   |  |  |    |                   |  |  |            |  |  |  |    |   |  |  |    |                             |  |  |            |   |  |  |         |                              |  |  |            |  |  |  |                                  |  |  |  |                    |
| <b>TOTAL OF ABOVE CALCULATIONS =</b>  |                              |  | \$ 1020.00                       |              |              |      |              |        |   |      |                    |       |   |      |   |  |   |    |                                      |  |  |            |   |  |  |    |                   |  |  |            |  |  |  |    |   |  |  |    |                             |  |  |            |   |  |  |         |                              |  |  |            |  |  |  |                                  |  |  |  |                    |
| <input checked="" type="checkbox"/> Applicant claims small entity status. See 37 CFR 1.27. The fees indicated above are reduced by ½.   |                              |  | \$                               |              |              |      |              |        |   |      |                    |       |   |      |   |  |   |    |                                      |  |  |            |   |  |  |    |                   |  |  |            |  |  |  |    |   |  |  |    |                             |  |  |            |   |  |  |         |                              |  |  |            |  |  |  |                                  |  |  |  |                    |
| <b>SUBTOTAL =</b>   |                              |  | \$ 1020.00                       |              |              |      |              |        |   |      |                    |       |   |      |   |  |   |    |                                      |  |  |            |   |  |  |    |                   |  |  |            |  |  |  |    |   |  |  |    |                             |  |  |            |   |  |  |         |                              |  |  |            |  |  |  |                                  |  |  |  |                    |
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| <input type="checkbox"/> 20 <input checked="" type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492 (f)). + _____   |                              |  | \$                               |              |              |      |              |        |   |      |                    |       |   |      |   |  |   |    |                                      |  |  |            |   |  |  |    |                   |  |  |            |  |  |  |    |   |  |  |    |                             |  |  |            |   |  |  |         |                              |  |  |            |  |  |  |                                  |  |  |  |                    |
| <b>TOTAL NATIONAL FEE =</b>   |                              |  | \$ 1020.00                       |              |              |      |              |        |   |      |                    |       |   |      |   |  |   |    |                                      |  |  |            |   |  |  |    |                   |  |  |            |  |  |  |    |   |  |  |    |                             |  |  |            |   |  |  |         |                              |  |  |            |  |  |  |                                  |  |  |  |                    |
| Fee for recording the enclosed assignment (37 CFR 1.21 (h)). Assignment Must be accompanied by appropriate cover sheet (37 CFR 3.28, 3.31) ( per property).   |                              |  | + \$ 00                          |              |              |      |              |        |   |      |                    |       |   |      |   |  |   |    |                                      |  |  |            |   |  |  |    |                   |  |  |            |  |  |  |    |   |  |  |    |                             |  |  |            |   |  |  |         |                              |  |  |            |  |  |  |                                  |  |  |  |                    |
| <b>TOTAL FEES ENCLOSED =</b>  |                              |  | \$ 1020.00                       |              |              |      |              |        |   |      |                    |       |   |      |   |  |   |    |                                      |  |  |            |   |  |  |    |                   |  |  |            |  |  |  |    |   |  |  |    |                             |  |  |            |   |  |  |         |                              |  |  |            |  |  |  |                                  |  |  |  |                    |
|   |                              |  | <b>Amount to be Refunded:</b> \$ |              |              |      |              |        |   |      |                    |       |   |      |   |  |   |    |                                      |  |  |            |   |  |  |    |                   |  |  |            |  |  |  |    |   |  |  |    |                             |  |  |            |   |  |  |         |                              |  |  |            |  |  |  |                                  |  |  |  |                    |
|   |                              |  | <b>Charged:</b> \$               |              |              |      |              |        |   |      |                    |       |   |      |   |  |   |    |                                      |  |  |            |   |  |  |    |                   |  |  |            |  |  |  |    |   |  |  |    |                             |  |  |            |   |  |  |         |                              |  |  |            |  |  |  |                                  |  |  |  |                    |
| a. <input checked="" type="checkbox"/> A check in the amount of \$ 1020.00 to cover the above fees is enclosed.   |                              |  |                                  |              |              |      |              |        |   |      |                    |       |   |      |   |  |   |    |                                      |  |  |            |   |  |  |    |                   |  |  |            |  |  |  |    |   |  |  |    |                             |  |  |            |   |  |  |         |                              |  |  |            |  |  |  |                                  |  |  |  |                    |
| b. <input type="checkbox"/> Please charge my Deposit Account No. 50-0624 in the amount of \$ _____ to cover the above fees. A duplicate copy of this sheet is enclosed.   |                              |  |                                  |              |              |      |              |        |   |      |                    |       |   |      |   |  |   |    |                                      |  |  |            |   |  |  |    |                   |  |  |            |  |  |  |    |   |  |  |    |                             |  |  |            |   |  |  |         |                              |  |  |            |  |  |  |                                  |  |  |  |                    |
| c. <input checked="" type="checkbox"/> The Commissioner is hereby authorized to charge any additional fees which may be required or credit Any overpayment to my Deposit Account No. 50-0624. A duplicate copy of this sheet is enclosed.   |                              |  |                                  |              |              |      |              |        |   |      |                    |       |   |      |   |  |   |    |                                      |  |  |            |   |  |  |    |                   |  |  |            |  |  |  |    |   |  |  |    |                             |  |  |            |   |  |  |         |                              |  |  |            |  |  |  |                                  |  |  |  |                    |
| <b>NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137 (a) or (b)) must be filed and granted to restore the application to pending status.</b>   |                              |  |                                  |              |              |      |              |        |   |      |                    |       |   |      |   |  |   |    |                                      |  |  |            |   |  |  |    |                   |  |  |            |  |  |  |    |   |  |  |    |                             |  |  |            |   |  |  |         |                              |  |  |            |  |  |  |                                  |  |  |  |                    |
| SEND ALL CORRESPONDENCE TO:   |                              | <br>SIGNATURE: _____<br>James R. Crawford<br>NAME: _____ |                                  |              |              |      |              |        |   |      |                    |       |   |      |   |  |   |    |                                      |  |  |            |   |  |  |    |                   |  |  |            |  |  |  |    |   |  |  |    |                             |  |  |            |   |  |  |         |                              |  |  |            |  |  |  |                                  |  |  |  |                    |
| James R. Crawford<br>FULBRIGHT & JAWORSKI L.L.P.<br>666 Fifth Avenue<br>New York, New York 10103<br>(212) 318-3148<br>Customer No. 24972  |                              | 39,155   |                                  |              |              |      |              |        |   |      |                    |       |   |      |   |  |   |    |                                      |  |  |            |   |  |  |    |                   |  |  |            |  |  |  |    |   |  |  |    |                             |  |  |            |   |  |  |         |                              |  |  |            |  |  |  |                                  |  |  |  |                    |

10/009099

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On DECEMBER 3, 2001

By: Eileen Sheffield

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DNAG-228

**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

Applicant(s) : Amirzadeh-Asl, et al.  
Based on: PCT/EP00/02872  
International Filing : March 31, 2000  
Date  
For : METHOD FOR PRODUCING BARIUM SULFATE, BARIUM  
SULFATE AND THE UTILIZATION THEREOF

Hon. Commissioner of Patents  
and Trademarks  
Washington, D.C. 20231 December 3, 2001

**PRELIMINARY AMENDMENT**

Sir:

Prior to prosecution, please amend the above-identified patent application as follows:

**IN THE CLAIMS:**

Cancel claims 1-7 without prejudice and substitute the following claims:

- 8.. Process for the continuous production of barium sulfate consisting of microcrystalline particles produced by precipitation, wherein a barium salt solution and a sulfate solution are simultaneously and continuously brought together in equimolar quantities in a precipitating suspension at a temperature of 30 to 90°C, with constant stirring, the precipitating suspension is withdrawn continuously in a steady volume and the barium sulfate precipitate is filtered, washed and optionally dried, wherein the barium salt solution has a concentration of 0.1 to 0.8 Ba<sup>2+</sup> mol/l and the sulfuric acid has a concentration of 0.1 to 2.0 SO<sub>4</sub><sup>2-</sup> mol/l, the flow rate and stirring speed being controlled, at a constant precipitation volume, in such a way that a pH value of 1 to 9 is obtained in the precipitating suspension.

9. Process according to claim 8, wherein a pH value of 1 to 5 is established in the precipitating suspension.
10. Process according to claim 8, wherein the withdrawn precipitating suspension is adjusted to a pH of 4 to 8 by addition of a base or acid.
11. Process according to claim 8, wherein the withdrawn precipitating suspension is adjusted to a pH of 4 to 7 by addition of a base.
12. Process according to claim 8, wherein that following the washing of the barium sulfate, an organic and/or inorganic aftertreatment of the barium sulfate in the precipitating suspension is carried out.
13. Barium sulfate, produced by a process wherein a barium salt solution and a sulfate solution are simultaneously and continuously brought together in equimolar quantities in a precipitating suspension at a temperature of 30 to 90°C, with constant stirring, the precipitating suspension is withdrawn continuously in a steady volume and the barium sulfate precipitate is filtered, washed and optionally dried, wherein the barium salt solution has a concentration of 0.1 to 0.8 Ba<sup>2+</sup> mol/l and the sulfuric acid has a concentration of 0.1 to 2.0 SO<sub>4</sub><sup>2-</sup> mol/l and the flow rate and stirring speed are controlled, at a constant precipitation volume, in such a way that a pH value of 1 to 9 is obtained in the precipitating suspension, wherein the lamellar particles are 0.1 to 50 µm wide, 0.1 to 50 µm long and 0.1 to 2 µm thick and the needle-shaped particles are 1 to 50 µm long and 0.1 to 2 µm thick, the ratio of length or width to the thickness being 3:1 to 500:1.
14. Use of the barium sulfate according to claim 13 as filler for thermosetting and thermoplastic plastics, elastomers, sealants, adhesives, fillers, varnishes, paints, cosmetics, paper, glass and as substrate for colored pigment formulations as well as for single-layer or multilayer coatings consisting of metal oxides, metal oxide mixtures and/or metal compounds, as a nucleus of crystallization for lead sulfate in the negative electrode paste of lead accumulators and as an X-ray contrast medium.

REMARKS

The purpose of this amendment is to conform the claims to standard U.S. practice.

Respectfully submitted,

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Process for producing barium sulfate, barium sulfate and  
use thereof

Description

5

This invention relates to a process for the continuous production of barium sulfate consisting of microcrystalline particles produced by precipitation, wherein a barium salt solution and a sulfate solution are simultaneously and continuously brought together in equimolar quantities at a temperature of 30 to 90°C, with constant stirring, the precipitating suspension is withdrawn continuously in a steady volume and the barium sulfate precipitate is filtered, washed and optionally dried.

15

Barium sulfate is precipitated out very rapidly, and consequently in finely divided state, as a sparingly soluble substance when solutions containing  $\text{Ba}^{2+}$  and  $\text{SO}_4^{2-}$  ions are brought together. The particle size can be influenced by controlling the nucleation rate and growth rate, for example, by varying the concentration, temperature and stirring speed. The precipitating agent is also influential in that, under otherwise identical precipitation conditions, a coarser barium sulfate precipitate is obtained by using free sulfuric acid than by using neutral sulfates (Ullmann, Second Edition, Volume 2, page 119).

20

Discontinuous precipitation, in which one component is placed in the precipitation vessel, is to be distinguished from continuous precipitation, in which both components of the precipitation reaction are introduced simultaneously into a precipitation vessel equipped with overflow or bottom outlet. As is generally known, the continuous process is technically and economically superior to the discontinuously operated process.

25

DE-A-2 246 818 discloses a continuous process for producing microcrystalline barium sulfate powder having an average particle size  $d_{50}$  of 0.01 to 20  $\mu\text{m}$ . In this process, equimolar quantities of  $\text{Ba}^{2+}$  and  $\text{SO}_4^{2-}$  ions and 5 0.1 to 2% barium sulfate nuclei (based on barium sulfate passed through) are fed simultaneously and continuously into a precipitation vessel at a temperature of between 50°C and 80°C, with slow stirring, and flow rate and stirring speed are controlled at a constant 10 precipitation volume, with the provision that the barium sulfate particles of the target particle size form sediment in the outlet of the precipitation vessel and the small barium sulfate particles remain in the upper zone of the precipitation vessel. The barium sulfate 15 precipitate is then filtered, washed, dried and ground.

The barium sulfate powder thus produced, which is referred to as "Blanc fixe" powder, has an average particle size  $d_{50}$  of 0.01 to 20  $\mu\text{m}$ ; the individual 20 particles are spherical in finely divided products and cubiform in coarse products.

EP-B 0 445 785 describes a process for producing barium sulfate having a lamellar crystal morphology, in which 25 the diameter-height ratio is 5 to 100  $\mu\text{m}$  and the ratio of the square of the circumference of the lamella to the surface area of the orthogonal production plane is 20:1 to 150:1. The crystal morphology is butterfly-shaped with one or two planes of symmetry vertical to the 30 lamellar plane and with a concave part disposed around its circumference. A starting material consisting of a solution of a barium salt having a barium ion concentration of 0.001 to 0.05 mol/l is added dropwise at a pH value of 1.0 to 5.0 and at a temperature of 50 to 100°C, in a ratio of 1:10 to 5:1, to a solution of a 35 sulfate having a sulfate ion concentration of 0.01 to 0.05 mol/l. Starting materials used include sodium

sulfate, barium nitrate, barium chloride, barium hydroxide, barium acetate. The barium sulfate produced in this way is reported to have high transparency and low coefficients of friction. The disadvantages of this  
5 barium sulfate, which is produced by the discontinuous method, are that the low concentrations of barium ions and of sulfate ions in the starting solutions result in a very low content of barium sulfate in the precipitating suspension, with the consequence that the  
10 throughput is low and hence the production involves considerable expense. Incidentally, the surfaces of the barium sulfate particles are uneven.

15 The object of the present invention is to organise the procedures described above in such a way that barium sulfate containing particles in the form of lamellae and/or needles having a defined size and even surfaces can be produced on the large scale with as little expense as possible.

20 This object is achieved by the combination of features set out in claim 1.

25 Preferred developments of these features are given in claims 2 to 5.

The lamellar particles of the barium sulfate are according to the invention 1 to 50  $\mu\text{m}$  wide, 1 to 50  $\mu\text{m}$  long and 0.1 to 2  $\mu\text{m}$  thick and the needle-shaped  
30 particles are 0.1 to 50  $\mu\text{m}$  long and 0.1 to 2  $\mu\text{m}$  thick, the ratio of length or width to the thickness being 3:1 to 500:1.

35 As the barium sulfate has a very low binder requirement accompanied by excellent dispersibility and possesses a low specific surface, it is usable in almost all lacquers and emulsion paints. High-gloss coatings which

- are resistant to flocculation in combination with other pigments can be produced. The barium sulfate exhibits a very high light reflectance in the visible region and the UV and IR region of the spectrum, so that it
- 5 maintains the original brilliance and the hue of the coloured pigments used. Because of the high purity, the barium sulfate can be used in the necessary materials and coatings which come into contact with food.
- 10 The barium sulfate according to the invention is acid- and alkali-resistant, insoluble in water and in organic media and, used as an inert filler, is lightfast and weather-resistant. These properties render the barium sulfate suitable for numerous applications, as set out
- 15 in claim 7.
- The barium sulfate can be dispersed exceptionally well in all plastics and increases their hardness and rigidity without impairing the toughness and the surface
- 20 quality. In addition, it results in a distinctly higher X-ray opacity, for example, for medical articles and toys. Moreover, the barium sulfate according to the invention is suitable for producing semiopaque colourings, for example, for lamp coverings.
- 25 Natural substrates such as mica, talc, bentonite, kaolin, et cetera are used for producing special pigments, such as pearl gloss pigments, anticorrosive pigments, conductive pigments and catalysts. In this
- 30 connection, for example, mica is used as substrate in the production of pearl gloss pigments for use in cosmetics, varnishes and paints and plastics. A disadvantage of these natural raw materials is that these cannot, like conventional pigments, be dispersed
- 35 by the action of high gravitational forces, as this results in a destruction of the lamellar structure. The barium sulfate lamellae according to the invention have

excellent stability, however, and can be used both as substrate and directly, where high stability of the lamellar form is required. Another advantage over the natural raw materials, when used as filler, is the  
5 extremely high purity.

The invention is explained in more detail below by means of some Examples.

- 10 Figure 1 shows a diagrammatic transverse section through a precipitation reactor for the preparation of a barium sulfate precipitating suspension,  
15 Figure 2 shows a scanning-electron micrograph of lamellar barium sulfate particles,  
Figure 3 shows a scanning-electron micrograph of lamellar barium sulfate particles.

#### First Example

20 3.6 l/h of  $\text{Ba}(\text{OH})_2$  solution having an ion concentration of 0.3  $\text{Ba}^{2+}$  mol/l is introduced at a temperature of 50°C through a pipe (5) and 0.7 l/h dilute sulfuric acid containing 1.5  $\text{SO}_4^{2-}$  mol/l is introduced through a  
25 pipe (6), continuously and simultaneously at constant volume, by means of metering pumps (not shown), into a tank (1) having a capacity of 5 l (diameter 160 mm, height 270 mm), in which the precipitation surface (2) of the precipitating suspension (3) is maintained at 80%  
30 of the capacity, with the stirrer (4) operating at constant speed. The dilute sulfuric acid is metered onto the surface (2) of the precipitating suspension (3), while the  $\text{Ba}(\text{OH})_2$  solution is introduced slightly above the base (7) of the tank (1). Through the controlled  
35 addition of the starting solutions, the precipitation is regulated in such a way that the pH value of the precipitating suspension is consistently 3 to 3.5. The

residence time is 56 min at a precipitation temperature of 40 to 45°C. The precipitating suspension, which contains approximately 60 g BaSO<sub>4</sub>/l, is continually withdrawn at constant volume from the tank via a pipe (8) at a level of 140 mm. In adjustment tanks (not shown) the precipitating suspension (3) is adjusted to a final pH value of 4 by the addition of Ba(OH)<sub>2</sub> solution; this is important for subsequent processing. The electrical conductivity of the barium sulfate produced in this way is approximately 110  $\mu$ S/cm at the pH value of 4. The precipitating suspension (3) is filtered through a porcelain nutsch and washed. After having been dried at 110°C, the barium sulfate has an average particle size ( $d_{50}$ ), determined by laser diffraction granulometry, of 8  $\mu$ m.

As may be seen in the scanning-electron micrograph in Figure 2, the barium sulfate particles are lamellar and exhibit a very smooth surface. The width of the particles varies between approximately 5 and 20  $\mu$ m and the thickness between 0.5 and 1  $\mu$ m. The ratio of width to thickness is 5:1 to 40:1.

#### Second Example

Corresponding to the procedure described in the first Example, 3 l per hour of Ba(OH)<sub>2</sub> solution having an ion concentration of 0.3 Ba<sup>2+</sup> mol/l, at a temperature of 50°C, and 1.2 l per hour of dilute sulfuric acid having an ion concentration of 1.1 SO<sub>4</sub><sup>2-</sup> mol/l, at a temperature of 30°C, are introduced continuously and at constant volume into the tank (1). The precipitation is regulated in such a way that the pH value of the precipitating suspension is between 2 and 2.5. A barium sulfate having an average particle size  $d_{50}$ , measured by laser diffraction granulometry, of 11  $\mu$ m is obtained at a precipitation temperature of 30°C and a residence time

of 57 min (Figure 3). The lamellar barium sulfate particles have a width of 5 to 25  $\mu\text{m}$  and a thickness of approximately 1  $\mu\text{m}$ . The ratio of width to thickness is 5:1 to 25:1.

Claims

1. Process for the continuous production of barium sulfate consisting of microcrystalline particles produced by precipitation, wherein a barium salt solution and a sulfate solution are simultaneously and continuously brought together in equimolar quantities in a precipitating suspension at a temperature of 30 to 90°C, with constant stirring, the precipitating suspension is withdrawn continuously in a steady volume and the barium sulfate precipitate is filtered, washed and optionally dried, characterised in that the barium salt solution has a concentration of 0.1 to 0.8 Ba<sup>2+</sup> mol/l and the sulfuric acid has a concentration of 0.1 to 2.0 SO<sub>4</sub><sup>2-</sup> mol/l, the flow rate and stirring speed being controlled, at a constant precipitation volume, in such a way that a pH value of 1 to 9 is obtained in the precipitating suspension.
2. Process according to claim 1, characterised in that a pH value of 1 to 5 is established in the precipitating suspension.
3. Process according to one of claims 1 and 2, characterised in that the withdrawn precipitating suspension is adjusted to a pH of 4 to 8 by addition of a base or acid.
4. Process according to claim 3, characterised in that the withdrawn precipitating suspension is adjusted to a pH of 4 to 7 by addition of a base.
5. Process according to one of claims 1 to 4, characterised in that following the washing of the barium sulfate, an organic and/or inorganic

aftertreatment of the barium sulfate in the precipitating suspension is carried out.

6. Barium sulfate, produced by a process wherein a  
5 barium salt solution and a sulfate solution are simultaneously and continuously brought together in equimolar quantities in a precipitating suspension at a temperature of 30 to 90°C, with constant stirring, the precipitating suspension is withdrawn  
10 continuously in a steady volume and the barium sulfate precipitate is filtered, washed and optionally dried, wherein the barium salt solution has a concentration of 0.1 to 0.8 Ba<sup>2+</sup> mol/l and the sulfuric acid has a concentration of 0.1 to 2.0  
15 SO<sub>4</sub><sup>2-</sup> mol/l and the flow rate and stirring speed are controlled, at a constant precipitation volume, in such a way that a pH value of 1 to 9 is obtained in the precipitating suspension, characterised in that the lamellar particles are 0.1 to 50 µm wide, 0.1 to 50 µm long and 0.1 to 2 µm thick and the needle-shaped particles are 1 to 50 µm long and 0.1 to 2 µm thick, the ratio of length or width to the thickness being 3:1 to 500:1.
- 25 7. Use of the barium sulfate according to claim 6 as filler for thermosetting and thermoplastic plastics, elastomers, sealants, adhesives, fillers, varnishes, paints, cosmetics, paper, glass and as substrate for coloured pigment formulations as well  
30 as for single-layer or multilayer coatings consisting of metal oxides, metal oxide mixtures and/or metal compounds, as a nucleus of crystallisation for lead sulfate in the negative electrode paste of lead accumulators and as an X-ray contrast medium.

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[Fortsetzung auf der nächsten Seite]

(54) Title: METHOD FOR PRODUCING BARIUM SULFATE, BARIUM SULFATE AND THE UTILIZATION THEREOF

(54) Bezeichnung: VERFAHREN ZUR HERSTELLUNG VON BARIUMSULFAT, BARIUMSULFAT UND VERWENDUNG DES BARIUMSULFATS



(57) Abstract: The invention relates to a method for the continuos production of micro-crystalline lead sulfate particles, whereby a barium salt solution and a sulfate solution are simultaneously brought into contact with each other in a precipitating suspension and constantly stirred, the precipitating suspension is continuously removed and the barium sulfate precipitation is filtered and washed. In order to produce flake-shaped and/or needle-shaped barium sulfate particles, the barium salt solution concentration ranges between 0.1 to 0.8 Ba<sup>2+</sup> mol/l and the sulfuric acid concentration ranges between 0.1 to 2.0 SO<sub>4</sub><sup>2-</sup> mol/l, whereby throughput and stirring speeds are adjusted at a constant precipitation volume in such a way that a pH value of 1 to 9 is obtained in the precipitating suspension.

(57) Zusammenfassung: Bei einem Verfahren zur kontinuierlichen Herstellung von mikrokristallinen Bleisulfat-Teilchen werden gleichzeitig Bariumsalz-Lösung mit Sulfatlösung in einer Fällsuspension unter konstanten Rühren zusammengebracht, die Fällsuspension kontinuierlich abgezogen und der Bariumsulfat-Niederschlag filtriert und gewaschen. Zur Herstellung plättchen-und/oder nadelförmiger Bariumsulfat-Teilchen besitzt die Bariumsalz-Lösung eine Konzentration von 0,1 bis 0,8 Ba<sup>2+</sup> mol/l und die Schwefelsäure eine Konzentration von 0,1 bis 2,0 SO<sub>4</sub><sup>2-</sup> mol/l, wobei der Durchsatz und die Rührgeschwindigkeiten bei konstant gehaltenem Fällvolumen so geregelt werden, daß in der Fällsuspension ein pH-Wert von 1 bis 9 vorliegt.

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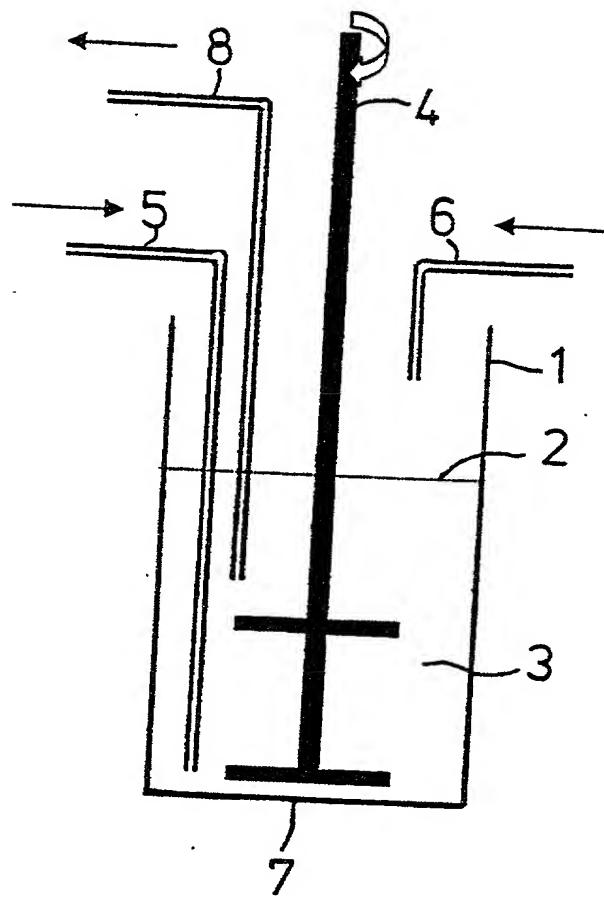


FIG. 1

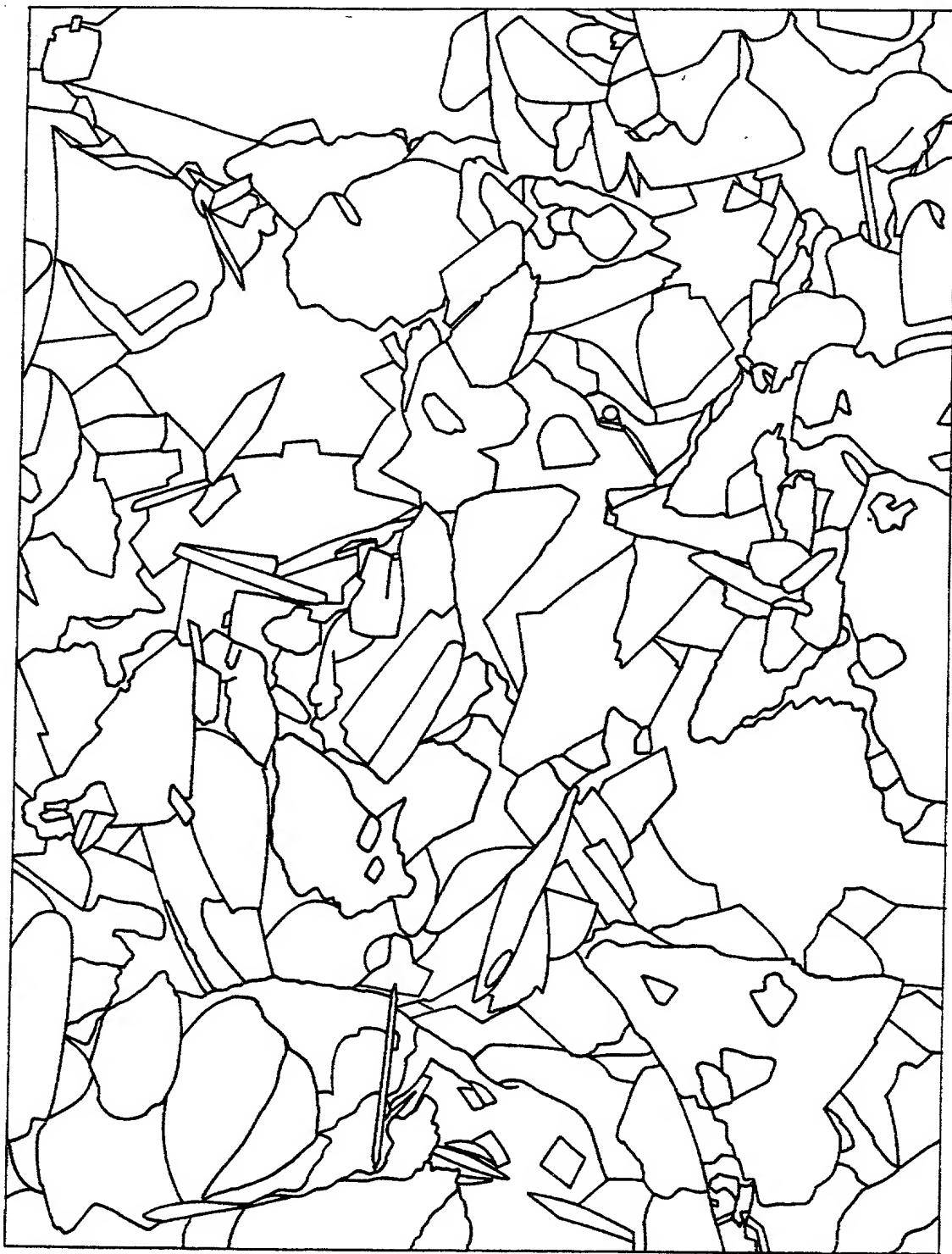
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Fig.2



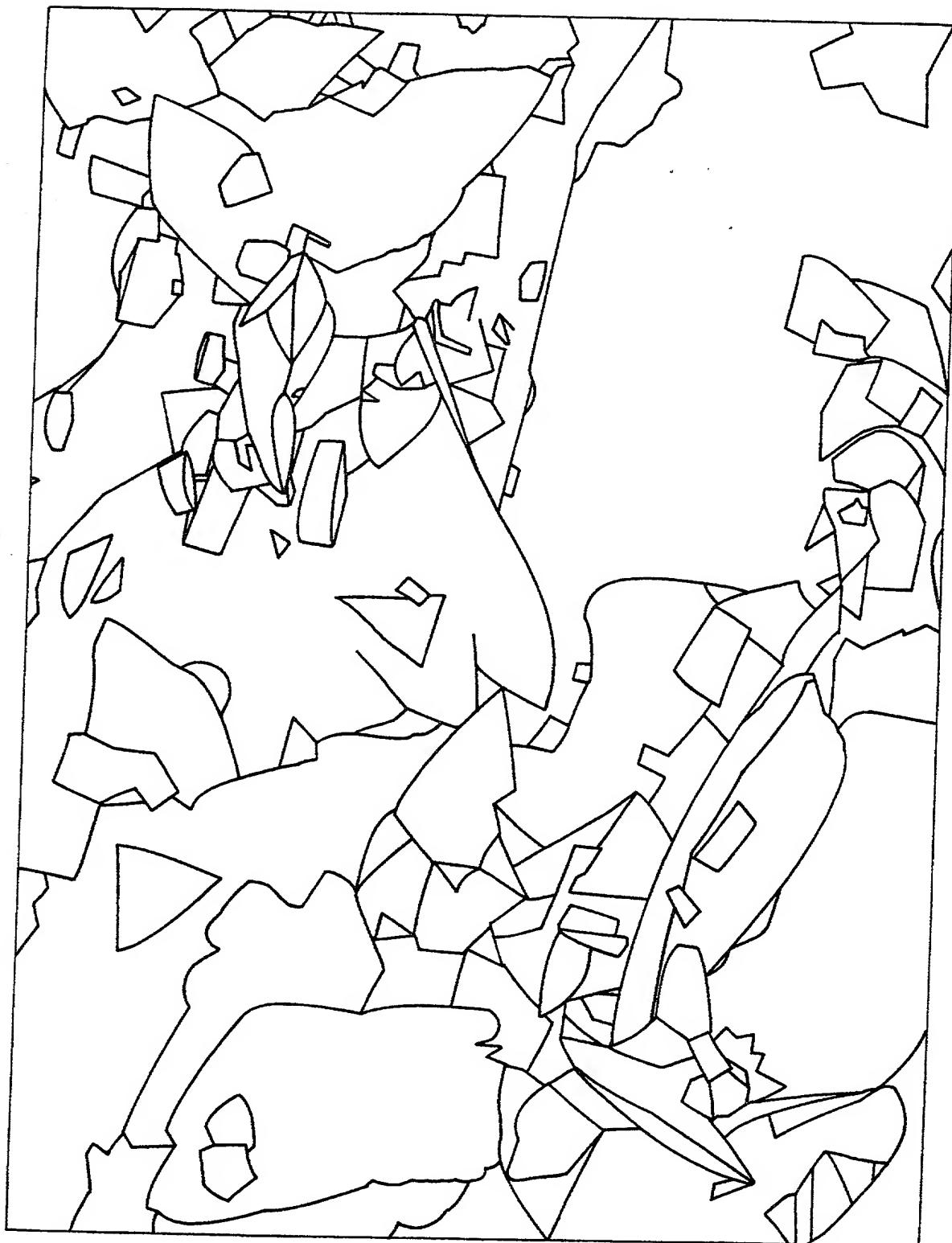
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Fig. 3





### DECLARATION/POWER OF ATTORNEY

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name.

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled

#### METHOD FOR PRODUCING BARIUM SULFATE, BARIUM SULFATE AND THE UTILIZATION THEREOF

the specification of which:

- ( ) is attached hereto.  
 ( X ) was filed on December 3, 2001 as U.S. Serial No. 10/009,099

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information which is material to the examination of this application in accordance with Title 37, Code of Federal Regulations, §1.56(a).

I hereby claim foreign priority benefits under Title 35, United States Code, Section 119 of any foreign application(s) for patent or inventor's certificate listed below and have also identified below any foreign application for patent or inventor's certificate having a filing date before that of the application on which priority is claimed:

|                          |                      |                                      |                                    |
|--------------------------|----------------------|--------------------------------------|------------------------------------|
| 199 26 216.0<br>(Number) | Germany<br>(Country) | 09/06/1999<br>(Day/Month/Year Filed) | Yes (X) No ( )<br>Priority Claimed |
|--------------------------|----------------------|--------------------------------------|------------------------------------|

|                            |                  |
|----------------------------|------------------|
| Yes ( ) No ( )<br>(Number) | Priority Claimed |
|----------------------------|------------------|

#### U.S. Priority Applications

I hereby claim the benefit under Title 35, United States Code, Section 120 of any United States application(s) listed below and, insofar as the subject matter of each of the claims of the application is not disclosed in the prior United States application in the manner provided by the first paragraph of Title 35, United States Code, Section 112, I acknowledge the duty to disclose material information as defined in Title 37, Code of Federal Regulations, Section §1.56(a) which occurred between the filing date of the prior application and the national or PCT international filing date of this application:

|                                 |                                 |                                     |
|---------------------------------|---------------------------------|-------------------------------------|
| <u>PCT/EP00/02872</u>           | <u>March 31, 2000</u>           | <u>Pending</u>                      |
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| (Applic. Serial No.)            | (Filing Date)                   | (Status patented/pending/abandoned) |

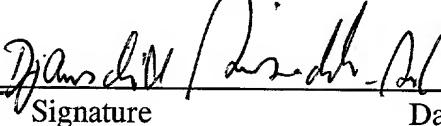
Power of Attorney

I hereby appoint the following attorneys to prosecute this application and transact all business in the Patent and Trademark Office connected therewith: Peter F. Felfe, Reg. No. 20,297; Norman D. Hanson, Reg. No. 30,946; John A. Bauer, Reg. No. 32,554; James Zubok, Reg. No. 38,671; James R. Crawford, Reg. No. 39,155; Andrew Im, Reg. No. 40,657, and David Rubin, Reg. No. 40,314, my attorneys with full power of substitution and revocation. Address all telephone calls to James R. Crawford, (212) 318-3148. Address all correspondence to James R. Crawford, Esq. at

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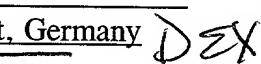
I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

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